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Dear Sir or Madam:

As required by 40 CFR 716, as amended, we herewith submit a copy of the following recently completed health and safety study.

Fate of TDI in Water, Part IV, Project FE-E-63

<u>Chemical Name</u>	<u>CAS Number</u>
2,4 Toluenediisocyanate	584-84-9
2,6 Toluenediisocyanate	91-08-7
Toluenediisocyanate (isomer mixture)	26471-62-5

The International Isocyanate Institute (III) reference number 11121 has been marked at the top of the title page of this report. Please refer to this III identification number in any communication regarding this study. **The enclosed report does not contain any Confidential Business Information.**

The study is sponsored by the International Isocyanate Institute on behalf of the following:

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FE-E-63-IV

11121

A Study of the fate of TDI in water

Effect of interfacial area under static condition

FE-E-63-IV

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Abstract

In order to complement and extend our earlier studies of the physico-chemistry of TDI/water interactions (Projects FE-E-63 parts I-III), the following two studies were carried out:

- (1) The effect of the interfacial area on the fate of 2,4-TDI in water under static condition

2,4-TDI, as a bottom layer in four cylindrical vessels of differing cross-sectional area, was immersed in water at 25°C, and the disappearance of 2,4-TDI and formation of water-soluble products were measured as a function of time over 15-30 days. The disappearance of 2,4-TDI followed zero-order kinetics and the rate increased with interfacial area. Six water-soluble reaction products including 2,4-TDA were observed by high performance liquid chromatograph (HPLC). The peak areas of these products and the dissolved organic carbon (DOC) of the test solution increased with the disappearance of 2,4-TDI and reached constant values. The final concentration of 2,4-TDA was larger with large interfacial area, while DOC was roughly independent on the interfacial area. The difference in concentration between DOC and 2,4-TDA, which was ascribed to the water-soluble reaction products other than 2,4-TDA, was independent on the interfacial area when the interfacial area was 5.7 cm² or above. The difference, however, in the interfacial area of 2.5 cm² was over 4 times larger than those for the area of 5.7 cm² or above.

The mechanism of the fate of 2,4-TDI in water and the prediction method of the concentration of the water-soluble reaction product formed from 2,4-TDI spilled in aquatic environment were discussed.

- (2) Identification of the water-soluble reaction product other than TDA observed in vigorous stirring experiment of 2,6-TDI

Water-soluble reaction product observed in vigorous stirring

experiment of 2,6-TDI was identified as monourea compound of 2,6-TDI (N,N'-di-(2-methyl-3-aminophenyl)urea) by liquid chromatograph - mass spectrometry (LC-MS).

1. Introduction

The International Isocyanate Institute has undertaken a major programme of human and environmental hazard assessment of TDI, a major industrial chemical used in polyurethane technology. This study forms part of a series of investigations on the physico-chemistry of TDI/water interactions. Clarification of these interactions is necessary in order to assess the ecotoxicological hazard of 2,4-TDI because isocyanate group has high reactivity to water.

Project FE-E-63 is designed to elucidate the fate of TDI in water. In earlier studies experiments were conducted on 2,4-TDI (T-100), 2,6-TDI (T-0) and the 80/20 mixture (T-80) under vigorously stirred and static conditions. The latter is closer to what are generally considered realistic conditions pertaining to an environmental spill, whilst the former gives a better indication of the homogeneous hydrolytic reactivity of 2,4-TDI. The results of these studies can be summarized briefly as:

- (1) With vigorously stirring the hydrolysis apparently followed first-order kinetics, the rate constant varying with initial TDI concentration, temperature, degree of agitation and salinity. Degradation under static conditions was considerably slower and followed zero-order kinetics.
- (2) Under both conditions the major products were generally water insoluble. Small amounts of water-soluble products of which a major component was TDA, were formed in the early stages of hydrolysis.

It is generally considered that the toxicity of TDI to aquatic organisms is caused mainly by the water-soluble reaction products, particularly TDA. Consequently, the effect of the aquatic environment of an accidental spillage of TDI could be evaluated if the production rate, amount and composition of water-soluble reaction product could be estimated from a knowledge of the controlling factors. The interfacial area between water and TDI phases is one of these factors because the water-soluble reaction products were assumed to be generated mainly by the reaction between water and TDI in the vicinity of this interface as discussed in the "Comprehensive Report of FE-E-63, Part I-III".

Since TDI under vigorous stirring is suspended as a particle, the interfacial area is roughly a function of the nominal concentration of TDI and therefore in studies FE-E-63 Parts I-III the disappearance rate of TDI and the amount of the water-soluble product, including TDA, were examined as a function of the nominal concentration of TDI. The same relationship, however, has not been examined in static experiment. One of the purpose of this study is to make clear the relationship between the interfacial area and the fate of 2,4-TDI in water, particularly the disappearance rate of 2,4-TDI, the production rate and amount of water-soluble reaction product, as a fundamental knowledge to assist evaluation of the hazard of TDI in aquatic environment.

Another purpose of this study is to identify the water-soluble reaction product from 2,6-TDI, which have not been identified in FE-E-63 Part III.

2. Materials and methods

2.1 Materials

The following materials were used;

- 2,4-TDI
Colocate T-100 (Nippon Polyurethane Industry Co., Ltd.)
Purity: 99.9%
- 2,6-TDI
supplied from International Isocyanate Institute (FE)
Purity: >99.8%
- 2,4-TDA
TCI-EP (Tokyo Chemical Industry Co., Ltd.)
Purity: >98%
- Water
distilled water (Takasugi Seiyaku Co., Ltd.)
- Acetonitrile
HPLC grade (Wako Pure Chemicals Inc.)

Other chemicals were of guaranteed reagent grade.

The standard solution of the dibutylamine derivative of 2,4-TDI was prepared as follows;

50.02mg (41.0 μ l) of 2,4-TDI was added to 15ml of toluene containing 37.5g dibutylamine per liter of toluene. After being allowed to stand for a few minutes, the solution was made up to 50ml with toluene. This solution was used as a stock solution and the standard solution for HPLC analysis was prepared by diluting the stock solution with acetonitrile.

The standard solution of 2,4-TDA was prepared by dissolving the fixed amount of the stock solution of 2,4-TDA in acetonitrile with water.

2.2 Methods

2.2.1 Study on the effect of the interfacial area on the fate of 2,4-TDI under static conditions

(1) Experimental methods

5g of 2,4-TDI was put into each of four cylinders differing in diameter (Table 1). The cylinders were immersed in tall beakers of 6cm diameter and 13cm height containing 300ml of water with caution, to prevent mixing of the lower TDI layer with the upper water layer. The beaker was placed in water thermostatted at 25°C. At appropriate intervals, about 20ml of the water phase was withdrawn with pipette and subjected to 2,4-TDA and DOC analysis. The inner small vessel containing 2,4-TDI was taken out and the water in it was joined with the residual water in the tall beaker. After the water was filtrated with filter paper, the residue was joined with 2,4-TDI in the inner small vessel and the residual amount of 2,4-TDI was measured according to the flow chart given in Figure 1.

Table 1. Characteristics of the inner vessels used in this study

No.	Shape	inner vessel		Height cm	Depth of TDI phase
		Diameter cm	Cross section cm ²		
A	Cylindrical	1.8	2.5	4.5	1.6
B	Cylindrical	2.7	5.7	4.1	0.72
C	Cylindrical	4.2	13.8	6.1	0.30
D	Cylindrical	5.0	19.6	7.0	0.21

Depth of TDI phase was calculated by the following equation;
Depth = $5/(g \times \text{cross section})$ where g is specific gravity (1.22).

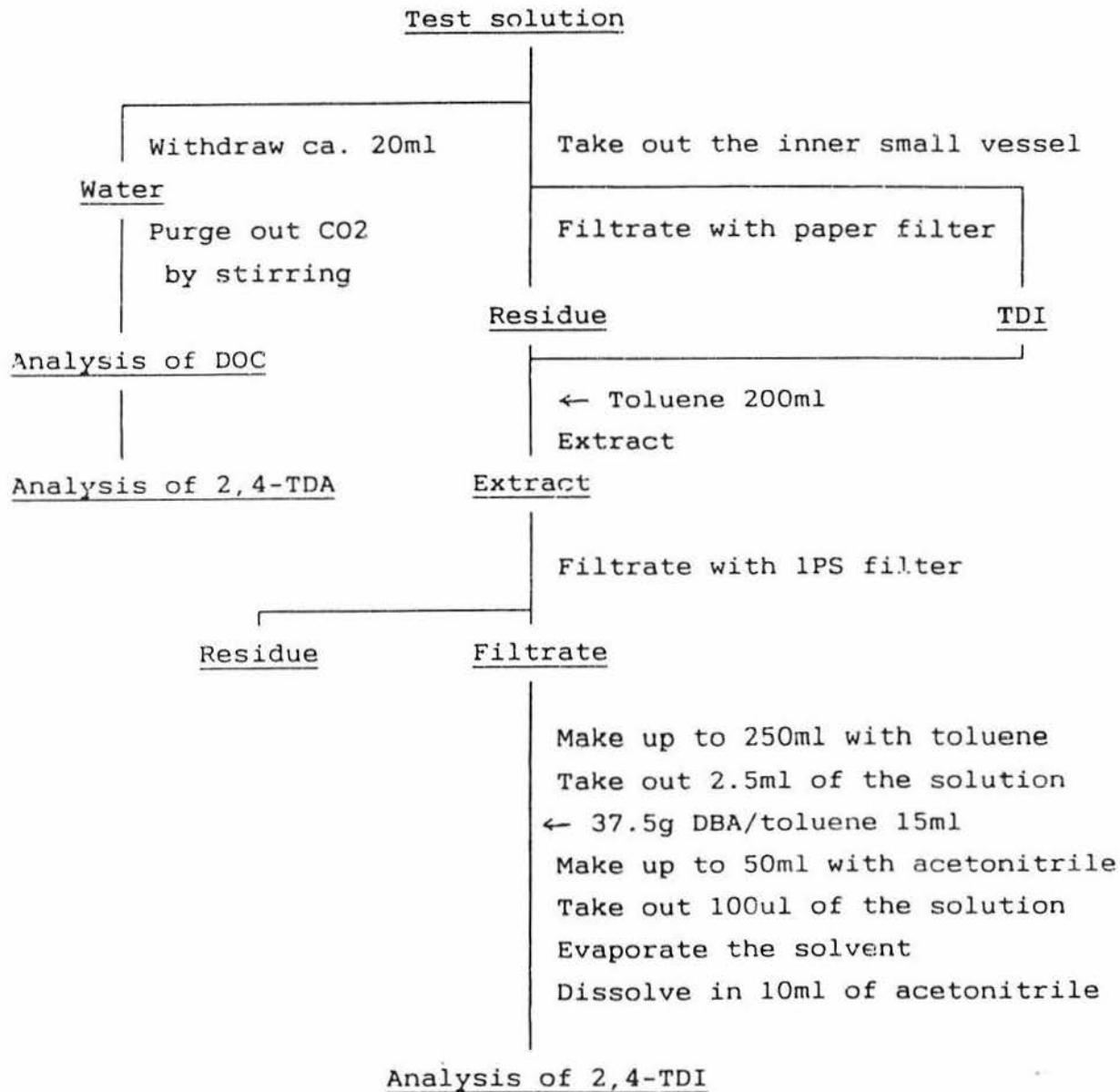


Figure 1. Flow chart for analysis of TDI, TDA and DOC

(2) Analytical conditions

- Analysis of the DBA derivative of 2,4-TDI

Apparatus : Shimadzu LC-6A
Column : L-column ODS (4.6mm ϕ x 15 cm Length)
(Chemicals Inspection & Testing Institute,
Japan)
Eluent : Acetonitrile/water = 4/1(v/v)
Flow rate : 1 ml/min
Detection : UV absorption
Wave length : 250 nm
Range : 0.01 AUFS
Injection vol.: 10 μ l

- Analysis of 2,4-TDA

Apparatus : Shimadzu LC-6A
Column : L-column ODS (4.6mm ϕ x 15 cm Length)
(Chemicals Inspection & Testing Institute,
Japan)
Eluent : Acetonitrile/water = 3/7(v/v)
Flow rate : 1 ml/min
Detection : UV absorption
Wave length : 230 nm
Range : 0.01 AUFS
Injection vol.: 10 μ l

- Analysis of DOC

Apparatus : Shimadzu total organic carbon analyzer
TOC-500
Furnace temp.: 680°C
Carrier gas : air
Flow rate : 150 ml/min
Inj. vol. : 10 μ l
Sensitivity : Range 3

2.2.2 Identification of water-soluble reaction product of 2,6-TDI

0.410ml (0.5g) of 2,6-TDI was added dropwise to 500 ml of water thermostatted at 25°C with stirring and was stirred for a further 15 days. After passed through a membrane filter, the filtrate was dried on a rotary evaporator. The resulting solid was dissolved in 2 ml of acetonitrile with the aid of ultrasonic irradiation and centrifuged at 3000 rpm for 10 minutes. The same operation was repeated with 1 ml of acetonitrile. The supernatant liquids were subjected to analysis of the water-soluble reaction product other than 2,6-TDA by liquid chromatograph-mass spectroscopy (LC-MC).

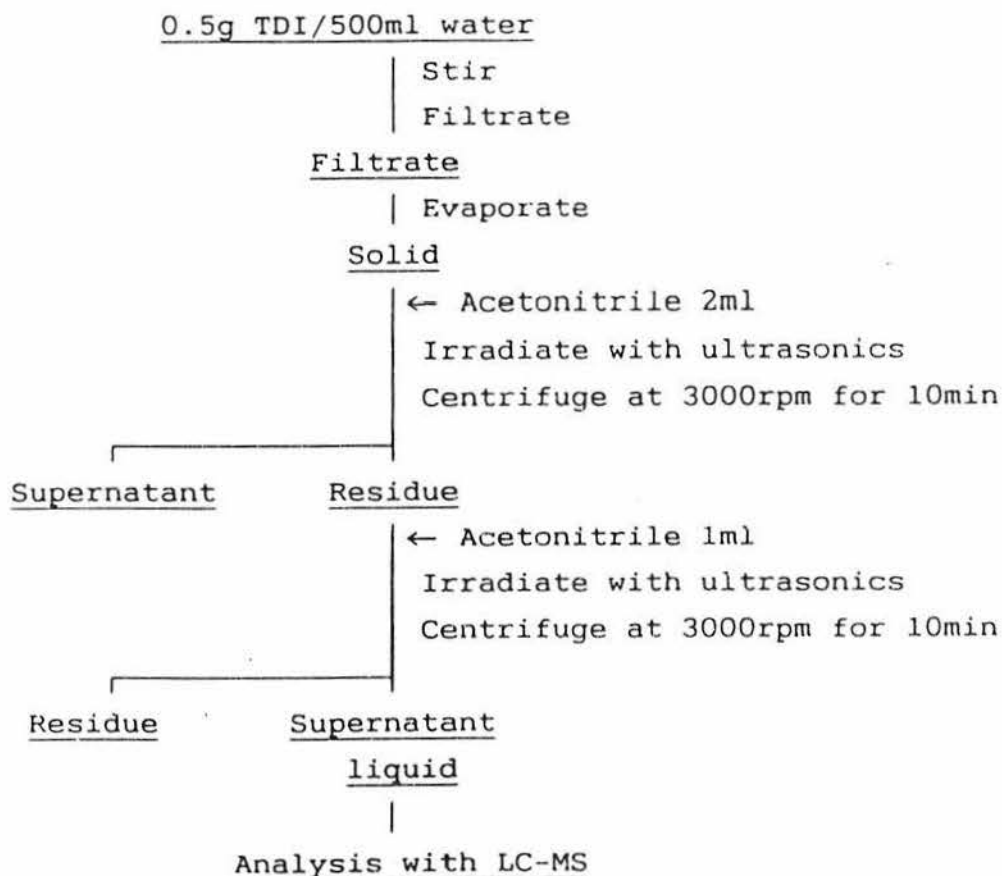


Figure 2. Flow chart of the identification of water-soluble reaction product of 2,6-TDI in water

The supernatant liquid after the first centrifugation contained a large proportion of 2,6-TDA and a small amount of other reaction products, but the latter components were concentrated by a factor of about 10 by repeating the operation (Figure 3).

The analytical conditions of LC-MS is as follows;

- Analytical conditions of LC-MS

Apparatus: Shimadzu LC/GC/QP1000S

HPLC conditions

Column : L-column ODS (4.6 ϕ x 15cm Length)
(Chemical Inspection & Testing Institute, Japan)

Eluent : Acetonitrile/water=3/7(v/v)
+ 50 mM CH₃COONH₄

Flow rate: 1ml + 0.3ml

Inj. vol.: 20 μ l

MS conditions

Ionization mode : Themospray

Detection mode : Positive and negative

Energy : 5.0 Rf gain : 495

Em gain : 4.0 Rf skew : 475

Monitoring Ion : m/z= 110 - 600

Temperature indicators ;

Block:650, TH : 630, Vaporizer : 648

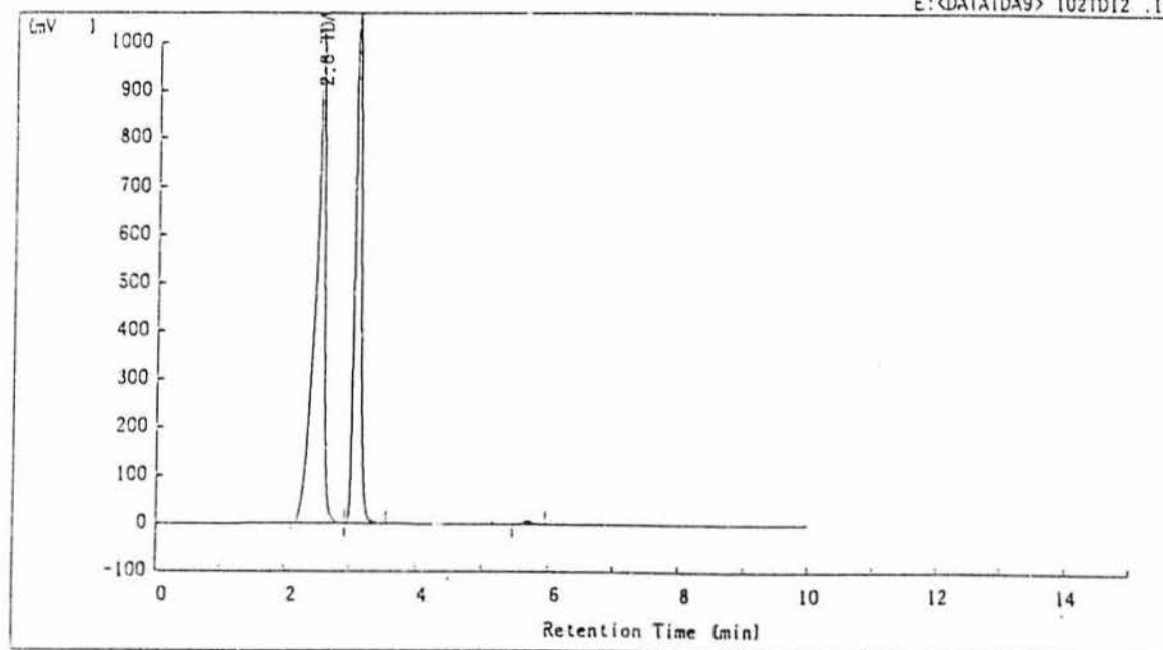
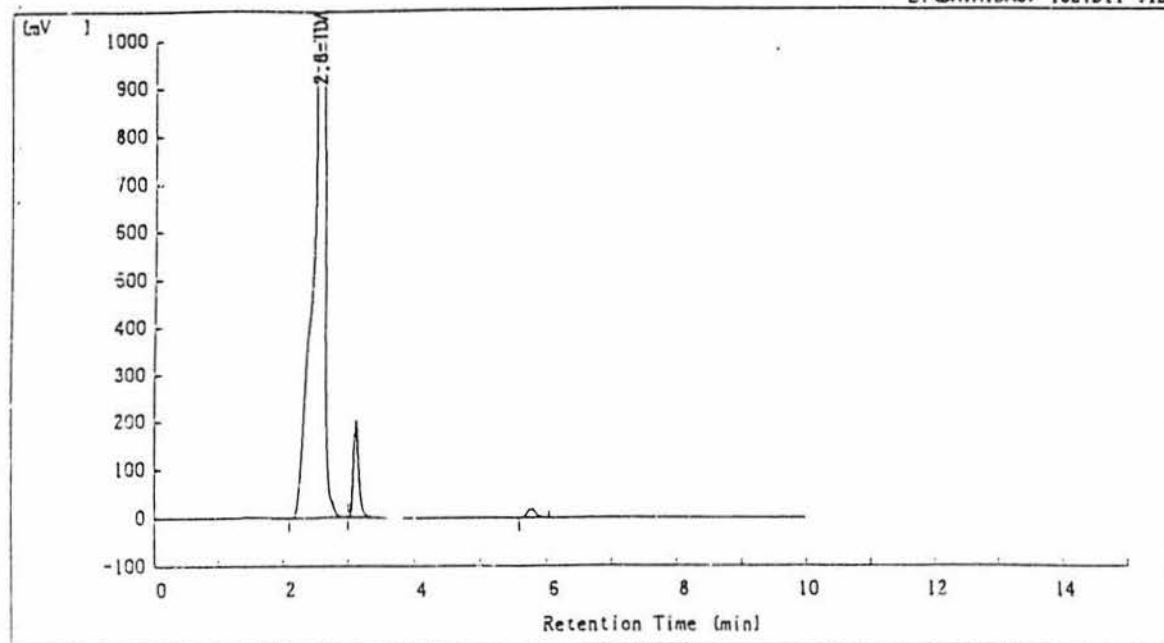


Figure 3. Chromatograms of water-soluble reaction products in the supernatant after the first (upper) and the second (bottom) concentration operations.

3. Results

3.1 Study on the effect of the interfacial area on the fate of 2,4-TDI under static conditions

(1) Disappearance of 2,4-TDI

The TDI layer changed in color from transparent to white with time. Typical chromatograms of the DBA derivatives of the residual 2,4-TDI are shown in Figure 4 and the residual curves of 2,4-TDI under four conditions are shown in Figure 5. The percent residue of 2,4-TDI decreased linearly with time as observed in the static experiments of the former studies (FE-E-63 Parts I-III) in all experiments except in the experiment using the inner small vessel of smallest interfacial area, where it decreased linearly with time until about 35% but the disappearance rate was slowed down thereafter. These results indicate that 2,4-TDI disappeared by zero-order kinetics at the initial stage. The zero-order disappearance rate constant of 2,4-TDI was calculated by fitting the linearly decreasing data to the following equation:

$$\% \text{Residue} = R_0 - kt$$

where k is the zero-order rate constant, t is time and R_0 is constant, Table 2 shows the values of k and R_0 determined by least-squares method for four experiments and the straight lines in Figure 5 show the regression curves.

Figure 6 shows the relationship between k and the interfacial area. The k value increased with increasing the interfacial area, indicating that the disappearance rate of 2,4-TDI became faster with increasing the interfacial area under static conditions.

Table 2. The zero-order rate constant, k , and R_0 value of the disappearance of 2,4-TDI determined by least-squares method and the determination coefficient, r^2 , for four experiments.

Exp. No.	Interfacial area cm^2	k %/day	R_0 %	r^2
1	2.5	3.47	94.9	0.933
2	5.7	4.98	93.9	0.947
3	13.8	8.20	98.2	0.993
4	19.6	8.61	97.5	0.993

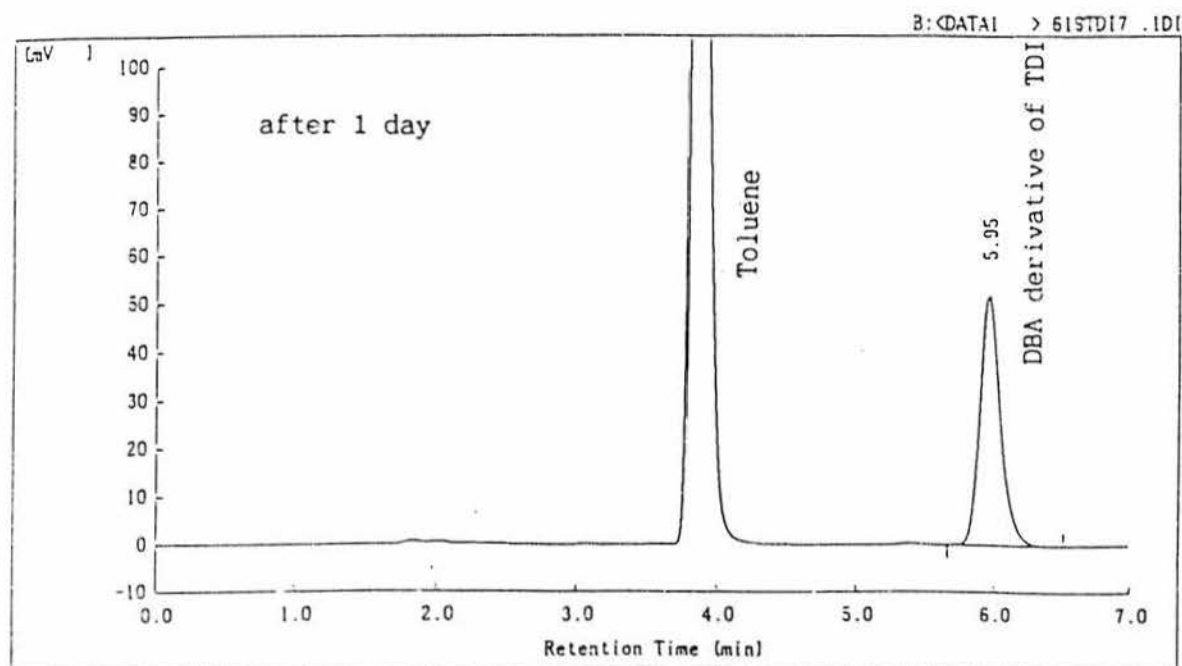


Figure 4. Typical chromatogram of DBA derivatives of residual 2,4-TDI. Cross section of the inner vessel = 19.6 cm^2 .

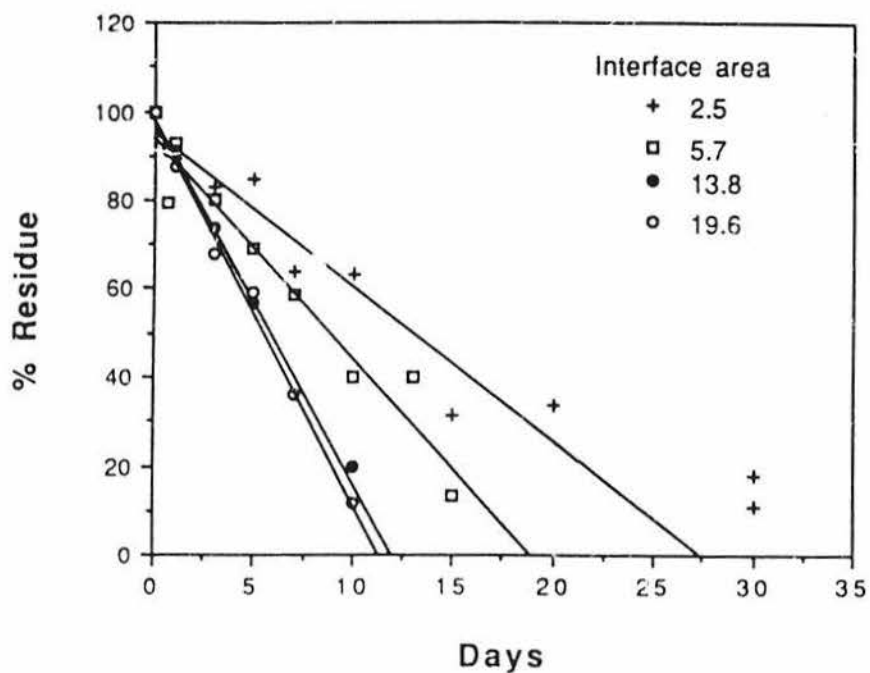


Figure 5. Residual curves of 2,4-TDI. The straight lines are the regression curves to zero-order kinetics.

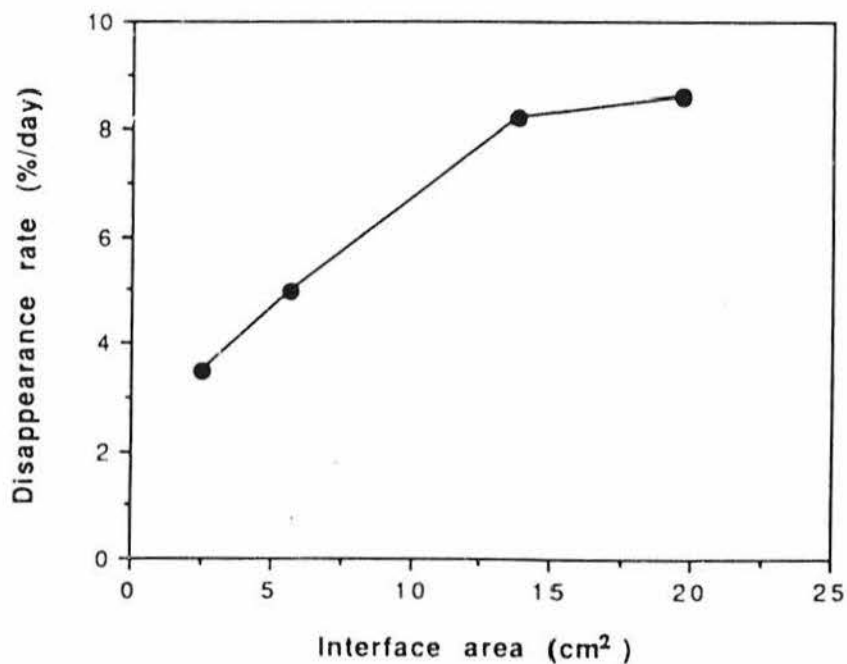


Figure 6. Relationship between the disappearance rate constant of 2,4-TDI and the interfacial area between TDI-water phases.

(2) Production of water-soluble reaction products

Water-soluble reaction products including 2,4-TDA were analyzed with HPLC and total organic carbon analyzer. The amount of 2,4-TDA was determined with HPLC. DOC in the water phase was measured to estimate total amount of water-soluble reaction products. The amount of the water-soluble reaction products other than 2,4-TDA was estimated from the difference in concentration between DOC and 2,4-TDA and from total peak area of the peaks other than 2,4-TDA observed with HPLC. The concentrations of DOC and 2,4-TDA, the difference concentration between DOC and 2,4-TDA and the total peak area excluding TDA peak were plotted against time. All values reached to constant values within test period. The final values were calculated by averaging two data at 7 and 10 days for the interfacial areas of 5.7, 13.8 and 19.6 cm² and by averaging three data at 15, 20 and 30 days for that of 2.5 cm² (Figures 8-11).

Figure 7 shows typical chromatograms of water-soluble reaction products. Six peaks including 2,4-TDA were observed on the same chromatogram. Figure 8 shows the production curves of 2,4-TDA under four conditions. 2,4-TDA increased with the disappearance of 2,4-TDI and reached to a constant value. The production rate of 2,4-TDA was faster and the final concentration of 2,4-TDA was larger with large interfacial area (Figure 8).

DOC in water phase also increased with decreasing residual TDI at nearly the same rate as 2,4-TDA and reached to a constant value, but the final concentration was roughly independent on the interfacial area (Figures 9). The amount of 2,4-TDA account for over 88% of the final DOC in the experiments using the inner small vessels of more than 5.7 cm² interfacial area, but it account for only 53% of total amount of the final DOC in the experiment of 2.5 cm² interfacial area.

Total concentration of water-soluble reaction products other than 2,4-TDA were estimated by subtracting the TDA concentration corrected by the carbon content from DOC. Figure 10 shows time course of the difference concentration between DOC and 2,4-TDA

and the relationship between the final value and interfacial area. When the interfacial area was 5.7 cm^2 or above, the difference concentration became the maximum values after 3 days, decreased thereafter and the final concentrations were not dependent on interfacial area, while in 2.5 cm^2 interfacial area, it increased until at least 7th-day and the final concentration at 30th-day was more than 4 times higher than those in larger interfacial areas. The amount of water-soluble products other than 2,4-TDA can be also estimated from the peak areas observed with HPLC. Five peaks with the retention times of 2.39, 4.15, 4.41, 5.10 and 5.90, respectively, were observed on the same chromatogram (Figure 7). Since these peaks, however, could not be quantified because of lack of standard solution, the relative peak area to the peak area of 10mg/l standard solution of 2,4-TDA was calculated to correct daily variation of response of the instrument and plotted with time in order to evaluate the variation pattern of the water-soluble reaction product other than 2,4-TDA. Figure 11 shows time course of relative total peak area of these peaks and the relationship between the final value and interfacial area. The time course of the total peak areas was similar to 2,4-TDA or DOC except the experiment using the inner small vessel of the smallest interfacial area, where the total area continued to increase after 10 days. The final value of total peak area other than 2,4-TDA exhibited the similar dependency on interfacial area to the difference concentration between DOC and TDA, suggesting the water-soluble reaction product other than 2,4-TDA are ascribed to the peaks observed with HPLC. As the main components of the peaks observed with HPLC are more retained substance on ODS column than 2,4-TDA, they are presumed to be the isomers of the oligourea of 2,4-TDI.

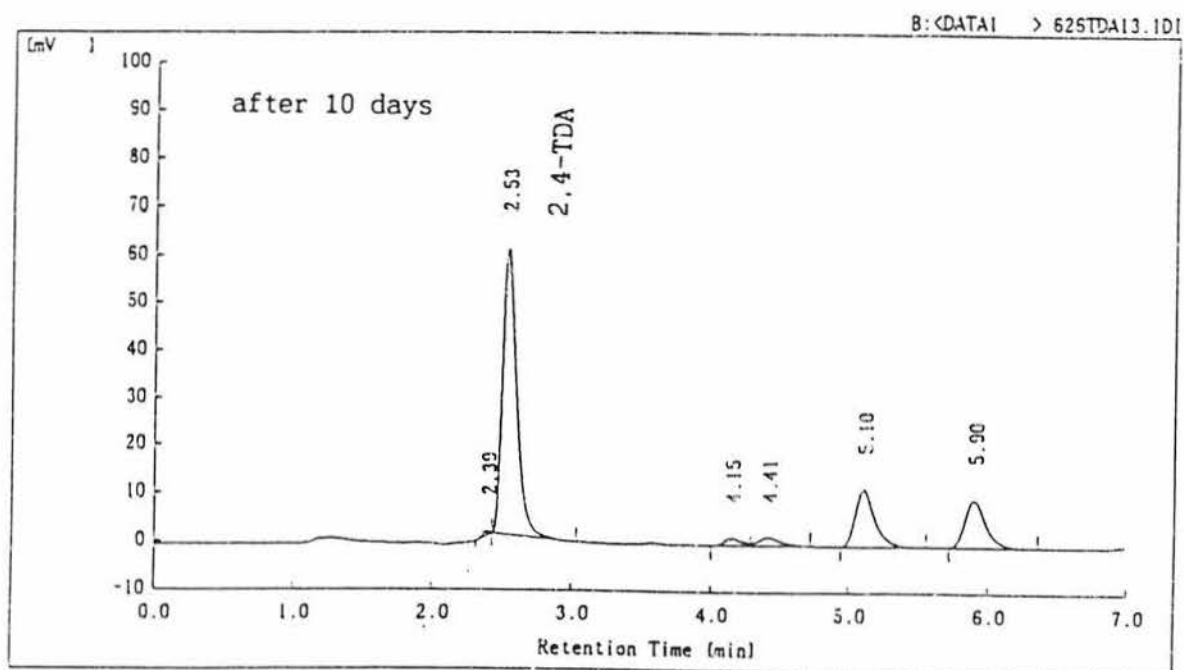
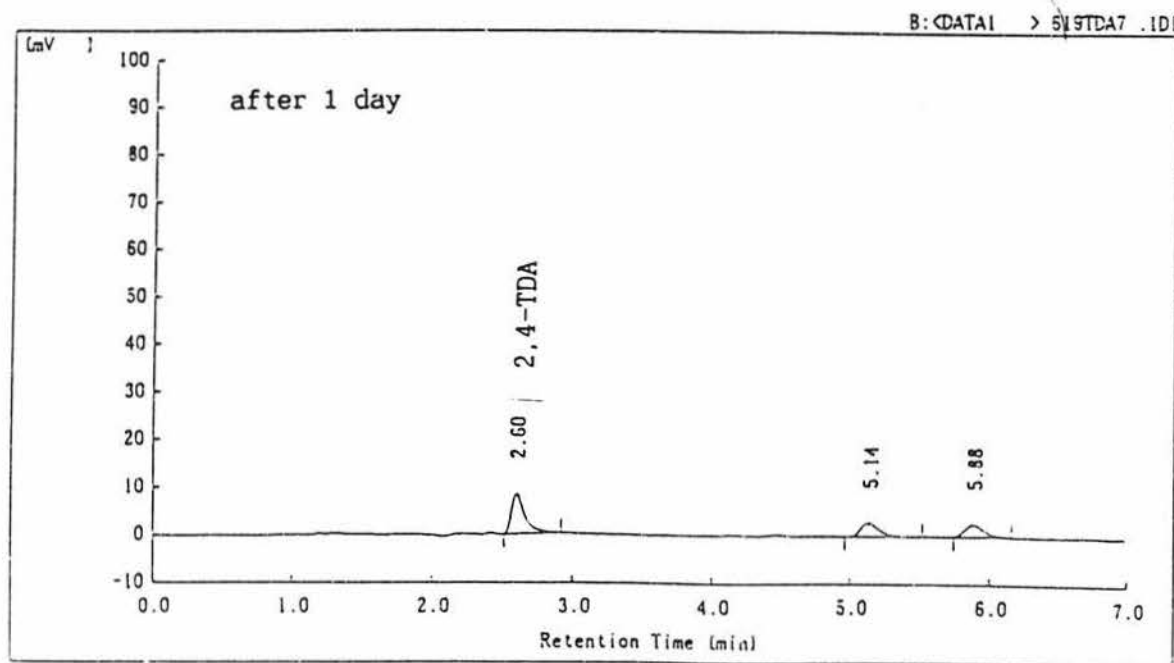


Figure 7. Typical chromatograms of water-soluble products of 2,4-TDI after 1 and 10 days under static conditions.
Cross section of the inner vessel = 19.6 cm^2

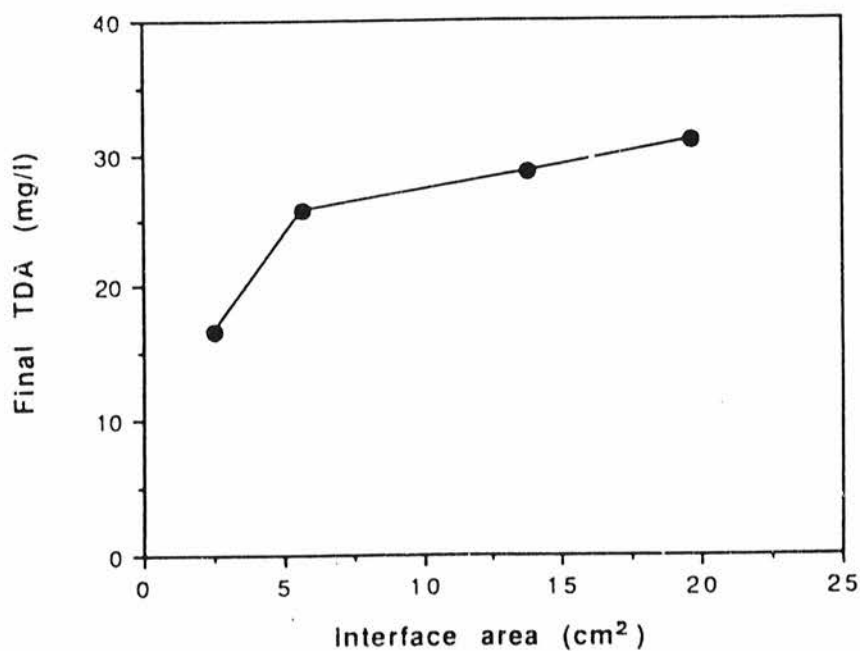
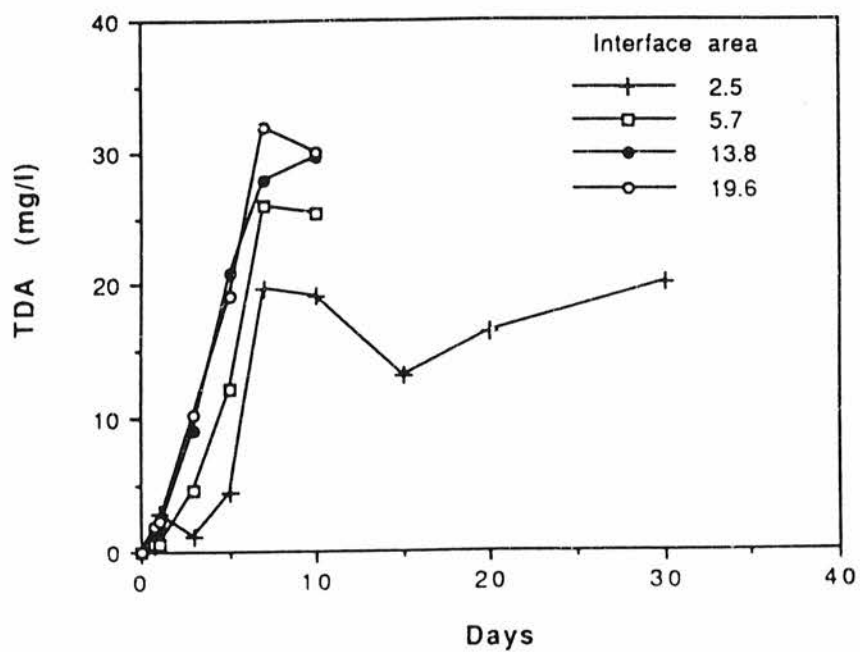


Figure 8. Production curves of 2,4-TDA (upper) and relationship between the final concentration and interfacial area (bottom).

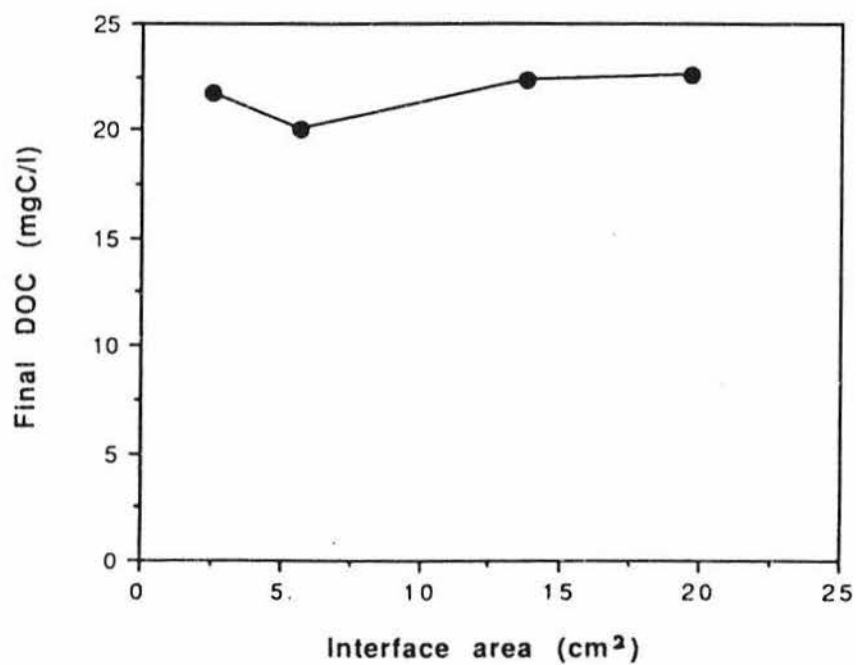
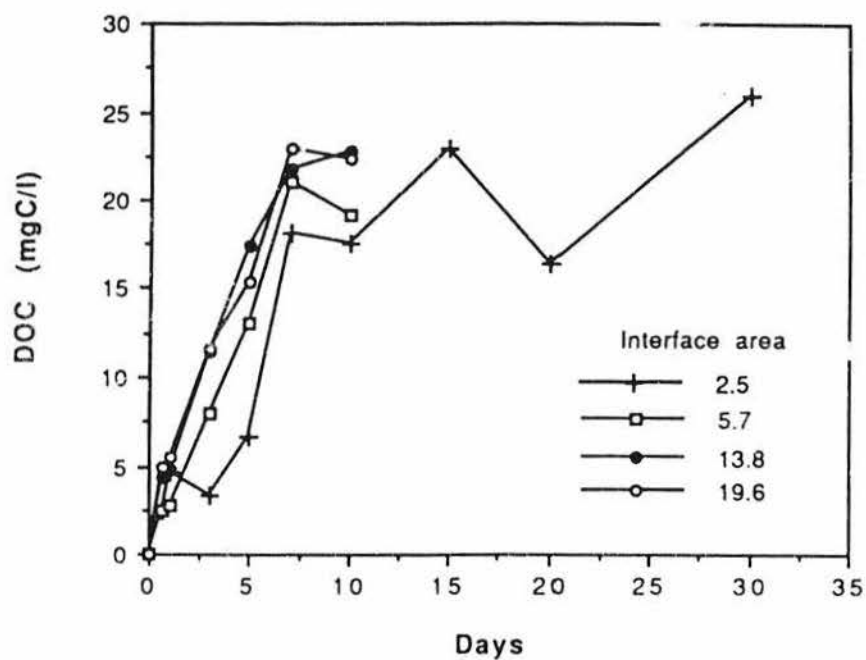


Figure 9. Production curves of DOC (upper) and relationship between the final DOC and interfacial area (bottom).

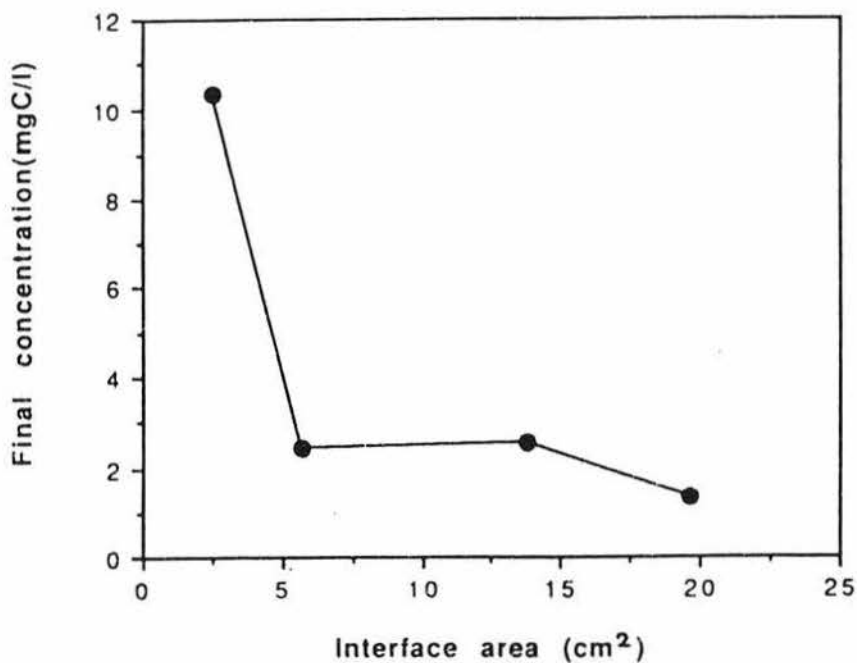
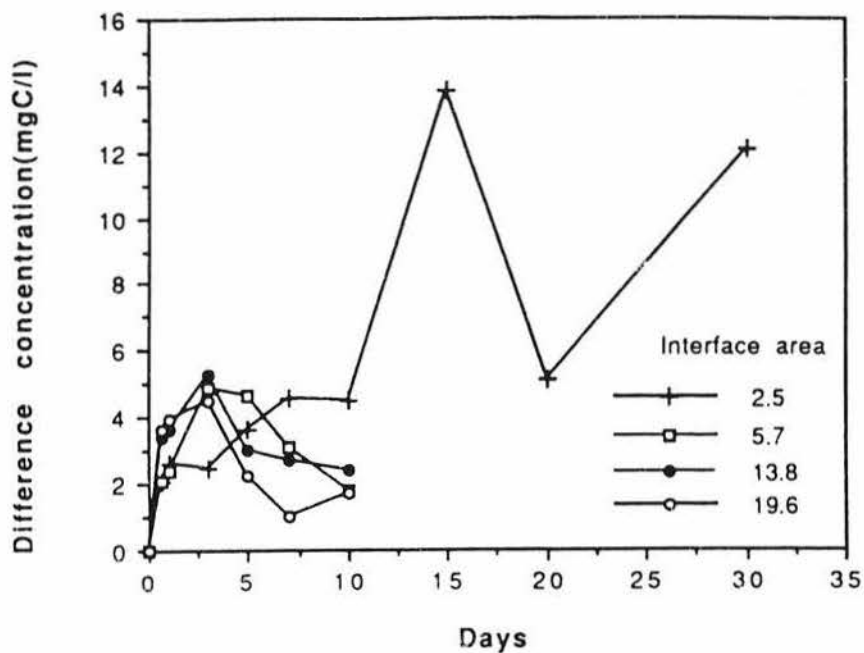


Figure 10. Difference concentration between DOC and TDA vs time plots (upper) and relationship between the final concentration and interfacial area (bottom).

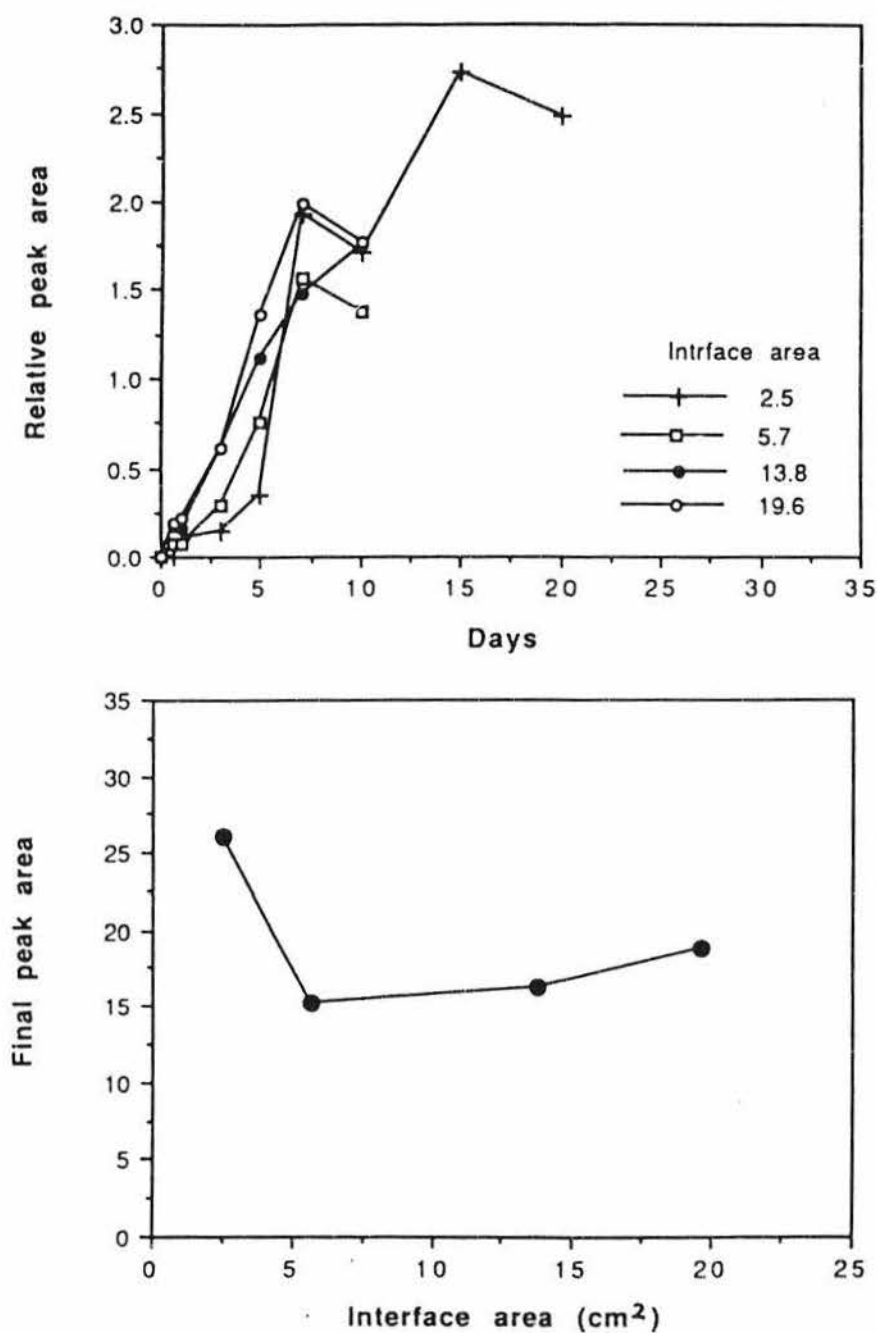


Figure 11. Relative total peak area of water-soluble products other than 2,4-TDA vs time plot (upper) and relationship between the final values and interfacial area (bottom). The relative peak areas were calculated by dividing the peak areas by that of 10 mg/l standard solution of 2,4-TDA.

3.2 Identification of water-soluble reaction product 2,6-TDI

Figure 12 shows the LC-MS spectra of the first peak apart from 2,6-TDA, in the water-soluble reaction product concentrated by the procedure in the Experimental section (Figure 3). The spectra were measured under two ionization modes, positive and negative. Both spectra indicate that the peak is monourea compound of 2,6-TDI, N,N'-di-(2-methyl-3-aminophenyl)urea. An additional peak was also observed, but was too small to allow identification.

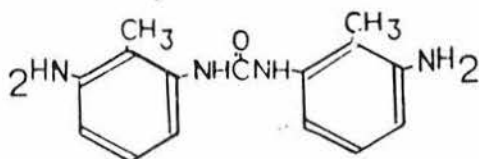
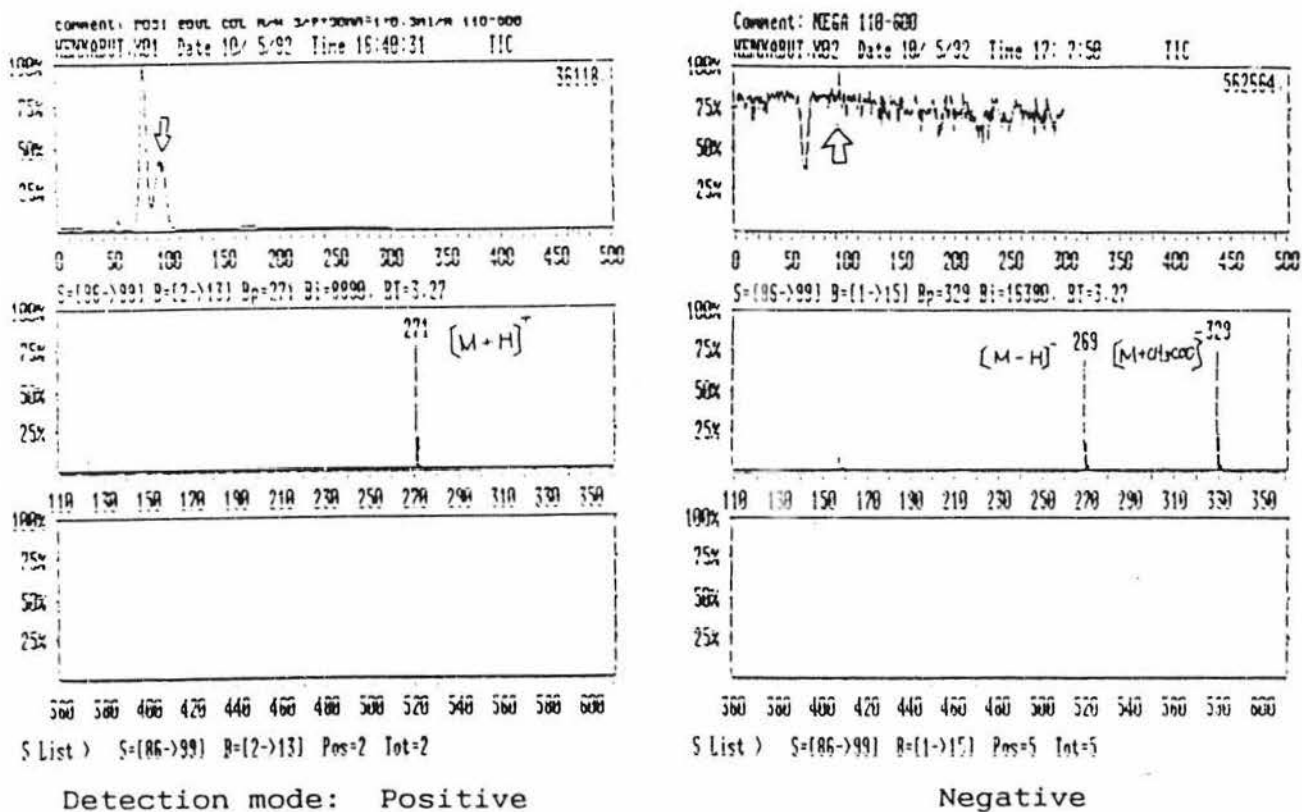


Figure 12. LC-MS spectra of water-soluble reaction product other than 2,6-TDA and the identified structure.

4. Discussion

The first step for the hazard assessment of TDI accidentally spilled in aquatic environment is to predict the concentration of hazardous substance. As discussed in "Comprehensive report of FE-E-63 project", it is thought that the disappearance of TDI is initiated by the reaction of TDI with the water permeated in TDI phase through the interface between TDI-water phases and the water-soluble reaction products are generated mainly from TDI in the vicinity of the interface because there is little possibility that the reaction product carrying amino group migrates from the inside of TDI phase far from the interface to the water phase without reacting with other isocyanate existing in TDI phase. These discussions indicate that the fate of TDI depends on the interfacial area between water-TDI phases and therefore clarification of the relationship between the fate of TDI and interfacial area is necessary for the hazard assessment of TDI.

In this section, we discuss the mechanism of the fate of 2,4-TDI in water and a method of prediction of the concentration of the water-soluble reaction products of TDI spilled under static condition on the basis of the present results.

(1) The mechanism of the interaction of 2,4-TDI with water

Since the disappearance of 2,4-TDI is initiated by the reaction with the water which has migrated from the water phase, the disappearance rate of 2,4-TDI is affected not only by the reaction rate between 2,4-TDI and water, but also by the permeation rate of water to 2,4-TDI phase. There are two extreme situations depending on the difference of the rates of both processes. If the rate of the former process is slower than the latter one, the reaction between 2,4-TDI and water occurs after the permeation of water to 2,4-TDI phase is completed, and the reaction presumably occurs homogeneously in the whole 2,4-TDI phase.

Alternatively, if 2,4-TDI reacts immediately after water permeates, then the reaction proceeds downwards from the TDI-water interface. In this case, it is expected that the reaction rate between 2,4-TDI and water will slow down as the reaction proceeds into 2,4-TDI phase, assuming that the reaction product of 2,4-TDI and water hinders the permeation of water. Such a decrease in the disappearance rate was observed in the experiment using the inner small vessel of the smallest diameter. This result supports the latter case.

However, the TDI phase changed in appearance from transparent to white color homogeneously throughout TDI phase under static condition. This observation can not be explainable by the latter mechanism.

Actual reaction is thought to proceed by the mixed mechanism of two cases. As an example, the following mechanism is supposed: the first reaction of 2,4-TDI and water in TDI phase is slower than the permeation rate of water to TDI phase and then it occurs homogeneously through TDI phase, but with proceeding the reaction, supply of water from the interface to the deep portion in the TDI phase become more difficult and consequently the reaction rate between 2,4-TDI and water is slowed down in deep portion. This mechanism, however, can not be verified completely from only available data.

(2) Predicted concentration of water-soluble reaction product.

As discussed above, it is thought that the water-soluble reaction products are generated in the TDI phase in the vicinity of the interface. This idea suggests that the amount of water-soluble reaction products should increase with increasing interfacial area. The result with 2,4-TDA is consistent with this expectation, but that with DOC is not. As was described in Section 3.1, if it is assumed that the remainder of DOC excluding 2,4-TDA is due to oligoureas then the dependence of DOC on interfacial area observed in this study indicates that large quanti-

ties of oligoureas were produced in the experiment using the inner small vessel of smaller surface area compared to the experiments using the inner small vessel of larger interfacial area. This might be explained if it is assumed that the oligourea compounds are produced mainly in the deeper portion of the TDI phase than 2,4-TDA. This assumption is plausible because 2,4-TDA produced in the deep portion of the TDI phase has more possibility to react with other TDI in the TDI phase and to be transformed to the oligourea during migration to the water phase compared to 2,4-TDA produced in the vicinity of interface, but further study is required to explain this phenomenon completely.

These discussions suggest that water-soluble reaction product is generated in the TDI phase within a fixed depth specific to kind of the product from the interface between TDI-water and therefore the amount of the product is dependent on not only the interfacial area between TDI-water phases, but also on the depth of TDI phase when the depth of the TDI phase used in experiment is smaller than the fixed depth. If such a fixed depth is assumed, it is anticipated that the amount of the water-soluble product generated from unit interfacial area increases and reaches the plateau value with increasing depth of TDI phase. The plateau value corresponds to the maximum production amount of the product per unit interfacial area. Figure 13 show the amounts per unit interfacial area of 2,4-TDA and the difference in concentration between DOC and TDA, which is total amount of water-soluble products other than 2,4-TDA, as a function of the depth of the TDI phase. It can be seen from Figure 13 that the amount per unit interfacial area of 2,4-TDA increased linearly with the depth of TDI phase from 0.21 to 0.72 cm, but it deviated downward from the linear line at the depth of 1.6 cm. This result suggests that the amount per unit interfacial area of 2,4-TDA reaches to plateau value. From these discussions, we can propose the prediction method shown in Figure 14 for the amount of 2,4-TDA produced from TDI spilled into aquatic environment, in which the maximum production amount of 2,4-TDA can be estimated by multiplying the surface area of the spilled TDI by the maximum production amount

per unit area ($= 2.5\text{mg}/\text{cm}^2$ for 2,4-TDA).

However the plateau value for the difference concentration between DOC and TDA, which is ascribed to total amount of the water-soluble reaction products other than 2,4-TDA, can not be determined because the values tended to increase at the maximum depth examined in this study. Further study is required to determine the plateau value for it.

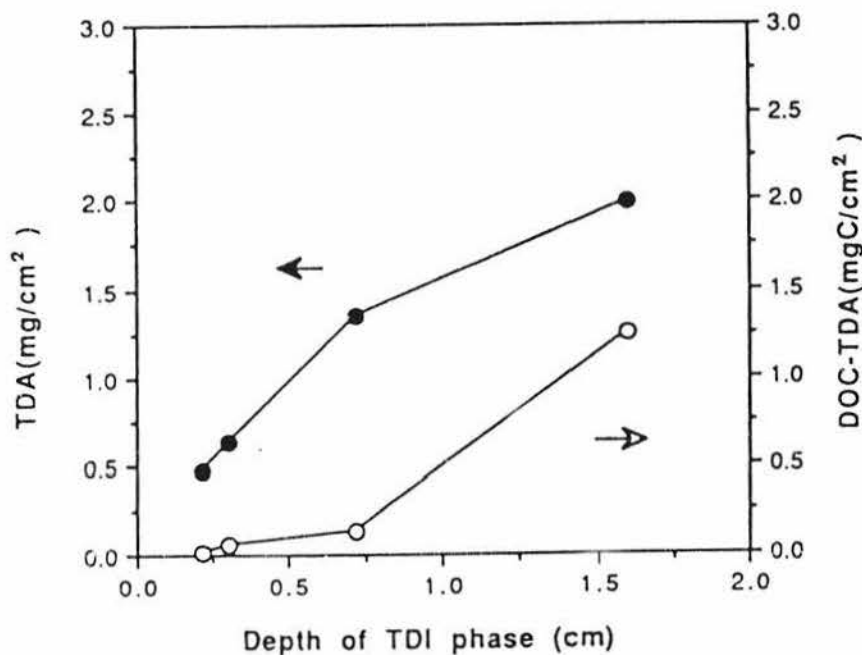


Figure 13. Relationship between 2,4-TDA, the difference concentration between DOC and 2,4-TDA per unit interfacial area and depth of the TDI phase.

$$\text{Maximum TDA (mg)} = P_u * A$$

$$\text{Maximum conc. of TDA (mg/l)} = \text{Maximum TDA} / V$$

where P_u : Maximum production per unit area of 2,4-TDA (mg/cm^2)

A : Interfacial area (cm^2)

V : Volume of water phase (liter)

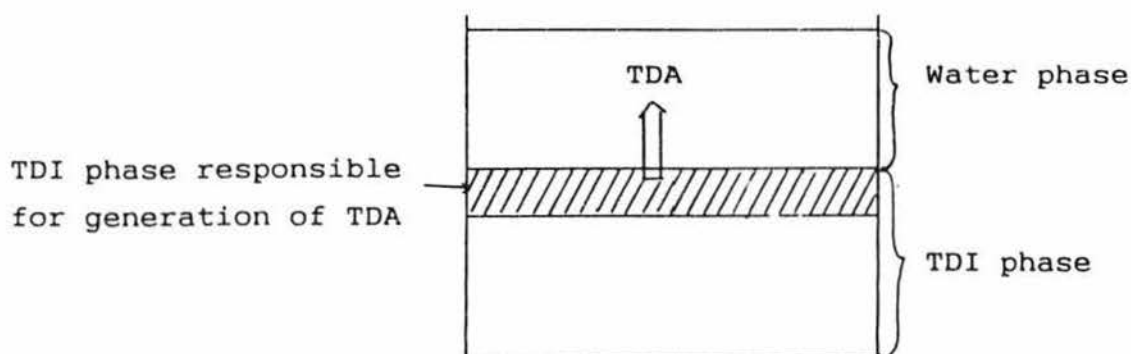


Figure 14. Proposed method for the prediction of the maximum production of 2,4-TDA from 2,4-TDI spilled into aquatic environment.

5. Reference

- (1) Bailey, R.E., Gilbert, D.S. and Kitahara, H. (1992). "Environmental Aspects of TDI", *Prog. Rubber Plast. Technol.*, 8:28-48.



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